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CONTRACT N00014-94-1-0101

R&T Code 31321075

Technical Report No. 10

INTRODUCTION TO LIVING POLYMERIZATION. LIVING AND/OR
CONTROLLED POYLMERIZATION

by

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Published

in the

J. Phys. Org. Chem., submitted

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June 30, 1994

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 30, 1994	3. REPORT TYPE AND DATES COVERED Technical Report # 10
4. TITLE AND SUBTITLE Introduction to Living Polymerization. Living and/or Controlled Polymerization			5. FUNDING NUMBERS N00014-94-1-0101
6. AUTHOR(S) Krzysztof Matyjaszewski			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Carnegie Mellon University Department of Chemistry 4400 Fifth Avenue Pittsburgh, PA 15213			8. PERFORMING ORGANIZATION REPORT NUMBER N00014-94-1-0101
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER Technical Report #10
11. SUPPLEMENTARY NOTES J. Phys. Org. Chem., submitted			
12a. DISTRIBUTION/AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) The effect of various imperfections such as slow initiation, termination, transfer and slow exchange on kinetics, molecular weights and polydispersities in chain growth polymerizations are simulated. The simulations demonstrate that well defined polymers can be prepared in systems with chain breaking reactions. Thus, under carefully selected conditions nonliving polymerization may provide controlled polymers. On the other hand, polymers with unpredicted molecular weights, broad and even polymodal molecular weight distributions can be formed in living systems without irreversible transfer and termination. In some living systems molecular weights may stay constant or even decrease with conversion. Thus, living and controlled polymerizations should be differentiated.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Classified	18. SECURITY CLASSIFICATION OF THIS PAGE Classified	19. SECURITY CLASSIFICATION OF ABSTRACT Classified	20. LIMITATION OF ABSTRACT UL

**Introduction to Living Polymerization.
Living and/or Controlled Polymerization.**

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Abstract:

The effect of various imperfections such as slow initiation, termination, transfer and slow exchange on kinetics, molecular weights and polydispersities in chain growth polymerizations are simulated. The simulations demonstrate that well defined polymers can be prepared in systems with chain breaking reactions. Thus, under carefully selected conditions nonliving polymerization may provide controlled polymers. On the other hand, polymers with unpredicted molecular weights, broad and even polymodal molecular weight distributions can be formed in living systems without irreversible transfer and termination. In some living systems molecular weights may stay constant or even decrease with conversion. Thus, living and controlled polymerizations should be differentiated.

Introduction

The term living polymerization was initially used to describe a chain polymerization in which chain breaking reactions were absent^{1,2}. In such an ideal system after initiation is completed, chains only propagate and do not undergo transfer or termination. Thus, in the ideal living polymerization each chain should retain its ability to react with monomer infinitely. However, transfer and termination often occur in real systems.

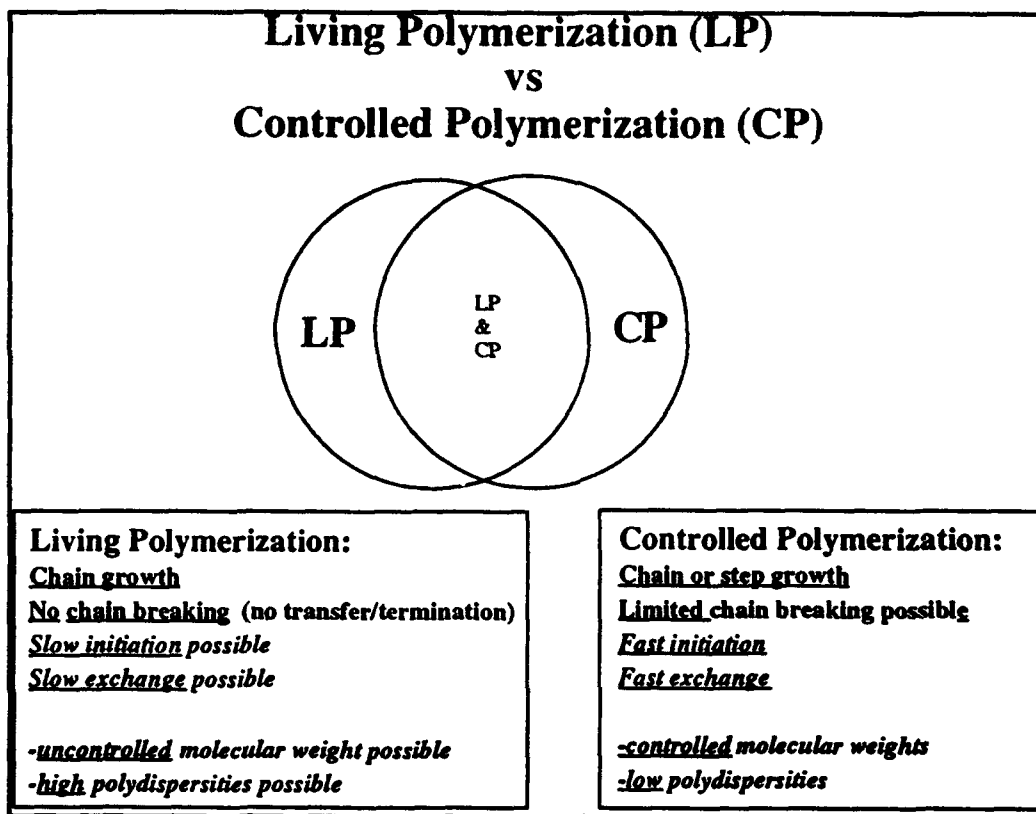
The number of papers describing living polymers, living catalysts (?), and living polymerizations is growing exponentially. Some of these processes will be discussed in other articles in this issue; some have been summarized in a recent review³ and will not be covered in this paper. Moreover, new terms such as quasi-living, semi-living, truly living, perfectly living, pseudoliving, apparently living, and immortal have been used, often without defining the term. Recently, some effort has been made^{4,5,6,7} to classify these systems and to establish criteria for living polymerizations. These criteria can be generally separated into kinetic and synthetic.

The intention of this paper is not to review existing and proclaimed living systems but to discuss the essence of a living polymerizations and to demonstrate that polymer properties are influenced by deviations from an ideal system. The importance of kinetics is stressed here and the effect of chain breaking reactions as well as slow initiation and slow exchange between species of different reactivities and lifetimes on rates, molecular weights and polydispersities is described quantitatively. These calculations show that well defined polymers can be prepared in the presence of chain breaking reactions. Thus, living polymerizations (no chain breaking reactions) and controlled polymerization (formation of well defined

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polymers) are two separate and not necessarily overlapping terms which should be distinguished and should not be confused.



Scheme 1. Comparison between Living and Controlled Polymerization

A **controlled** polymerization is defined here as a synthetic method for preparing polymers with predetermined molecular weights ($DP_n = \Delta[M]/[I]_0$), low polydispersity, controlled functionality, block copolymers, etc. Transfer and termination is allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

On the other hand, a **living** polymerization is defined as a chain polymerization without irreversible transfer and termination. Living

polymerizations will lead to well-defined polymers only if the following additional prerequisites are fulfilled:

- initiation is fast in comparison with propagation,
- exchange between species of different reactivities is fast in comparison with propagation,
- rate of depropagation is low in comparison with propagation
- system is sufficiently homogeneous, in sense of the availability of active centers and mixing.

If these specifications are not met, living polymerizations will produce polymers with broader polydispersities and degrees of polymerization much higher than the $\Delta[M]/[I]_0$ ratio.

The proportion of chains affected by transfer and termination increases with the chain length. As discussed later, this may not cause much deviation from ideal behavior (linear increase of M_n with conversion, very narrow polydispersities) if the chains are sufficiently short. Such systems have often been called living. However, if attempts at preparing higher molecular weight polymers under otherwise identical conditions (initiator, additive, solvent, temperature, etc.) are unsuccessful and if chain breaking reactions are indicated by a nonlinear evolution of molecular weights with conversion, and by variation of polydispersities and polymerization kinetics, then such a system should not be called living. The terms *apparently living* or "*living*" polymerization terms have been used previously to name systems which produced well-defined polymers of relatively low molecular weight but in which either transfer or termination are unambiguously present.^{8,9} The term **controlled polymerization** is a more accurate description of these systems.

It was proposed that the rate constants of transfer and termination or their ratios to that of propagation should be determined for polymerization systems which produce well-defined polymers⁷. This will enable reproducible syntheses in which the limits for the preparation of well defined high polymers are set. The transfer/termination rate constants may be detectable only by working under "difficult" reaction conditions which prevent preparation of well defined polymers (higher temperatures, lower $[I]_0$, longer chains, etc.). These results can then be extrapolated to the "usual living" conditions.

Systems with reversible transfer or reversible termination deserve special comment, since they have often been called pseudoliving or quasi-living. The first living systems were anionic polymerizations of non-polar monomers such as styrene and dienes in some hydrocarbon solvents. They showed perfectly living behavior producing very high molecular weight polymers ($M_n \gg 100,000$) with low polydispersities ($M_w/M_n < 1.1$), providing that initiation and mixing were fast enough^{10,11,12}. Polymerization resumes with the same rate after addition of a new portion of monomer with a linear increase of molecular weight with conversion. In addition, block copolymers form by consecutive polymerization of two comonomers. In these systems various active species coexist, including ions, ion pairs of various structures and reactivities, as well as their aggregates. Reactivities of ions are sometimes much higher than those of ion pairs ($k_p^-/k_p^\pm \approx 10^5$ in polymerization of styrene with Li^+ counterion in THF at 20 °C),^{2, 10,11,12} and in some cases ionic aggregates are much less reactive than ion pairs. Nevertheless, polymers with degrees of polymerization determined by the ratio of the concentration of reacted monomer to the overall concentration of active species or of introduced initiator ($DP_n = \Delta[M]/[I]_0$) have been

prepared with the narrow molecular weight distributions. This observation indicates that growing species with different reactivities exchange rapidly enough to give the same probability of growth for all chains. This also implies that the temporary decrease in activity (or temporary deactivation) does not interfere with the concept of a living polymerization. Thus, temporary deactivation is not considered termination. The same reasoning can be applied to reversible transfer and it has been suggested that both systems can be simply called living.⁶ The dynamics of the exchange reactions and the chain lengths are very important in both cases as discussed later.

Deviations from Ideal System

A general kinetic scheme for a typical chain polymerization is shown in Scheme 2. Initiation (1) usually proceeds by reaction of initiator (I) with monomer (M) to produce the first growing species (P_1^*). This species propagates (2A) with a rate constant which may be different from that of the macromolecular species (2B). Reaction of the growing species with monomer may also lead to transfer to monomer to generate new chains (3A). Transfer (3B) may also occur with a transfer agent (A). If the new species (A^*) have similar or higher reactivity than the growing species, there will be no effect on the kinetics. If the reactivity of A^* is lower than P^* , then degradative transfer occurs with retardation of the polymerization.

1)	$I + M \xrightarrow{k_i} P_1^*$
2A)	$P_1^* + M \xrightarrow{k_{p1}} P_2^*$
2B)	$P_n^* + M \xrightarrow{k_p} P_{n+1}^*$
3A)	$P_n^* + M \xrightarrow{k_{trM}} P_n + P_1^*$
3B)	$P_n^* + A \xrightarrow{k_{trA}} P_n + A^*$
4A)	$P_n^* \xrightarrow{k_t} P_n$
4B)	$P_n^* + T \xrightarrow{k_{tT}} P_n - T$
4C)	$P_n^* + P_m^* \xrightarrow{k_{tc}} P_n - P_m$
4D)	$P_n^* + P_m^* \xrightarrow{k_{td}} P_n + P_m^=$
5A)	$P_n^* \xrightleftharpoons[k_{\#*}]{k_{\#}} P_n^{\#}$
5B)	$P_n^{\#} + M \xrightarrow{k_p^{\#}} P_{n+1}^{\#}$
5C)	$P_n^* + P_m - A \xrightleftharpoons{k_{ex}} P_n - A + P_m^*$

Scheme 2. Kinetic Scheme for Chain Polymerization

Growing species may lose reactivity by spontaneous unimolecular termination (4A) or by bimolecular termination (4B) with a terminating agent (T). In radical polymerization bimolecular termination occurs by coupling (4C) or by disproportionation (4D). Growing species (P^*) may be in equilibrium (5A) with species $P^\#$ of different reactivity, which is also capable of reacting with monomer (5B). If species $P^\#$ can not react directly with monomer, then it is considered inactive and the termination step (4A) should be reversible. The last reaction (5C) is a degenerative transfer in which both the total number of chains capable of growth ($P_n^* + P_{m-A}$) and the concentration of active chains stay constant (P_n^*). This thermodynamically neutral process ($K=1$) may lead to polymers with narrow molecular weight distribution.

The simplest system which is both living and controlled involves only reaction 2; reactions 3-5 should be absent. As shown later, well defined polymers still can be formed if the contribution of these reactions is small and the degrees of polymerization is limited. However, living polymerization which involve slow initiation (1) will increase polydispersities and produce polymers of "too high" molecular weights. If initiation is faster or comparable to propagation, then reaction 1 (and 2A) can be omitted. Multiplicity of growing species with various reactivities and various lifetimes may produce polymers with broad and even polymodal molecular weight distributions. However, Poisson distributions result if exchange reactions (5A) are fast.

In the following sections the quantitative deviations of the kinetics, molecular weights and polydispersities from those of ideal systems caused by reactions 1,3,4,5 will be presented. The magnitude of only one deviation

will be varied at a time to clearly demonstrate the effect of slow initiation, termination, transfer, and slow exchange on polymerization rates and properties of the produced polymers.

1. Slow Initiation.

The effect of slow initiation on kinetics is shown in Fig. 1 for a hypothetical system in which only reactions 1 and 2B (Scheme 2) participate and with the following conditions $[M]_0=1$ mol/L, $[I]_0=0.01$ mol/L, $k_p=1$ mol⁻¹·L·s⁻¹.

Fig. 1

The kinetics is first order in monomer and should provide a straight line in semilogarithmic coordinates if the concentration of active sites is constant (instantaneous initiation). The time scale is defined by the product of the concentration of the propagating species and the rate constant of propagation, but the shape of the plot depends on the ratio of the rate constants of propagation to that of initiation. For the particular ratio $[M]_0/[I]_0=100$, no detectable deviation from the ideal law is found for $R_i=k_p/k_i=1$. If $R_i=10$, the initiator is nearly consumed at approximately 40% monomer conversion. On the other hand, at $R=30$ and 100, the unreacted initiator remains even at complete monomer consumption. Thus, continuous accelerations in the semilogarithmic coordinates is observed.

It is even easier to notice the effect of slow initiation by analyzing the evolution of molecular weight with conversion in Figs. 2 and 3.

Fig.2

The small increase in the polymerization degree relative to the ideal case disappears at approximately 40% conversion when $R_i=10$. However, it is necessary to add subsequent portions of monomer (conversions >100%) for

ratios $R_i=30$ and $R_i=100$ to approach asymptotically ideal M_n values as shown in Fig. 3.

Fig. 3

Polydispersities in systems with slow initiation depend on the ratio $[M]_0/[I]_0$ and R_i , and are very narrow for $R_i=1$ and 10 ($M_w/M_n < 1.02$) but approach $M_w/M_n=1.15$ for the ratio $R_i=100$. The highest polydispersity due to slow initiation is $M_w/M_n=1.3$ ¹³. The effect of slow initiation on kinetics, molecular weights and polydispersities has been discussed before in detail for general systems^{2,13,14,15} and for the carbocationic polymerization.¹⁶

2. Termination.

The effect of termination was studied for a hypothetical system in which only reactions 2B and 4A (Scheme 2) participate. Termination has no effect on the final number average molecular weights because it does not change the total number of chains. Of course, termination may lead to incomplete polymerization if the initiator concentration is too low. If termination is unimolecular the final monomer conversion ($[M]_\infty$) is set by eq. 1.

$$\ln([M]_0/[M]_\infty)=[I]_0(k_p/k_t) \quad (1)$$

Thus, the effect of termination is mostly kinetic as shown in Fig. 4.

Fig. 4.

Fig. 4 depicts the semilogarithmic plots for various ratios $R_t=k_p/k_t$, taking arbitrary values of $k_p=1 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$, $[M]_0=1 \text{ mol/L}$, $[I]_0=0.001 \text{ mol/L}$, and assuming instantaneous initiation.

For the ratios $R_t=100,000$ and $10,000$ nearly no deviation from the ideal behavior is observed and complete conversions, predicted molecular weights and polydispersities lower than $M_w/M_n < 1.03$ are calculated. On the other hand, if $R_t=1,000$, 63% conversion is expected at infinite time. Calculations predict $DP_n=630$ and $M_w/M_n \approx 1.45$ for the final product. The effect of termination on molecular weight distribution has been discussed thoroughly in ref. 17,18,19. Bimolecular termination with a terminating agent T obeys a pseudofirst order kinetics if $[T] \gg [P^*]$.

3. Termination in Radical Polymerization

The growing species in radical polymerization terminate by either disproportionation or coupling. Most radical polymerization systems involve slow initiation and a very low stationary concentration of radicals in order to prepare polymers of sufficiently high molecular weights. Therefore, in most systems only a small fraction of the initiator is used, and the rate of initiation is approximately constant (decomposition of the initiator by light, high temperature or redox process is usually the rate determining step, $r_i = k_d \cdot [I]_0$). The number average degree of polymerization depends on the ratio of the rate of propagation to that of the initiation and termination. Both the propagation rate and the polymerization degree decrease with conversion as shown in Fig. 5. The arbitrarily chosen conditions ($[M]_0=10 \text{ mol/L}$, $r_i=10^{-7} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, $k_p=10^2 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, and $k_t=10^7 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$) are close to those for the bulk polymerization of styrene at 60°C initiated by AIBN.

Fig.5.

The polydispersity increase with conversion from the normal value $M_w/M_n=1.5$ for termination by coupling to $M_w/M_n=2.5$ at 95% conversion.

This is due to the change in the ratio of the rate of propagation to that of initiation, according to eq.(2)¹⁷:

$$\begin{aligned}
 DP_n &= \frac{2([M]_0 - [M]) \cdot k_p}{\ln([M]_0/[M]) \cdot (2r_i \cdot k_t)^{1/2}} \\
 DP_w &= \frac{3([M]_0 + [M]) \cdot k_p}{2 \cdot (2r_i \cdot k_t)^{1/2}}
 \end{aligned}
 \tag{2}$$

A similar dependence is predicted for termination by disproportionation, although the initial polydispersities are higher ($M_w/M_n=2$).

4. Transfer

Ideally, transfer has no effect on kinetics, but does have a pronounced effect on molecular weights and polydispersities.^{17,18,20} Fig. 6 shows the effect of transfer to monomer on the polymerization degree for various ratios $R_{trM}=k_p/k_{trM}$, using arbitrary concentrations $[M]_0=1$ mol/L, $[I]_0=0.01$ mol/L, and assuming that initiation is instantaneous and termination is absent.

Fig. 6

Instead of the predicted final $DP_n=100$, smaller values are computed ($DP=91, 75$ and 50) when $R_{trM}=1000, 300$, and 100 , respectively. Notice that the deviation from $\Delta [M] / [I]$ is smaller at lower DP and increases at higher DP range for each R_{trM} value.

As shown in Fig. 7, this deviation depends not only on R , but also on the ratio of the concentrations of monomer to that of initiator, which can be expressed by the parameter $a = (k_{trM}/k_p) \cdot [M]_0/[I]_0$, as shown in eq. 3.

$$DP/DP^{id} = 1 / \{ 1 + (k_{trM}/k_p) \cdot [M]_0/[I]_0 \cdot p \} \quad (3)$$

The ratio of the degree of polymerization in the presence of transfer to that predicted for the ideal system without transfer ($DP^{id} = \Delta[M]/[I]_0$) decreases with conversion⁹.

Fig. 7

For the initial conditions $[M]_0 = 1$ mol/L, $[I]_0 = 0.01$ mol/L, and $R_{trM} = k_p/k_{trM} = 1000$, 10 % deviation from ideal behavior is expected (case $a = 0.1$). At complete conversion a decrease in the initiator concentration to $[I]_0 = 0.001$ mol/L ($a = 1$) leads to DP one half the ideally predicted value whereas $[I]_0 = 0.0001$ mol/L ($a = 1$) leads to one tenth that value. However, nearly ideal behavior can be reached with $[I]_0 = 0.1$ mol/L. This shows that in systems dominated by transfer it is possible to improve polymerization control by simply manipulating (increasing) the initiator concentration.

Fig. 8 depicts the predicted effect of the parameter a on the polydispersities²⁰.

Fig. 8

Using $[M]_0 = 1$ mol/L, $[I]_0 = 0.01$ mol/L, a polydispersity of $M_w/M_n \approx 1.06$ is expected for the ratio $k_p/k_{trM} = 1000$. Decreasing the initiator concentration to $[I]_0 = 0.001$ mol/L leads to $M_w/M_n \approx 1.5$, whereas increasing $[I]_0$ to 0.01 mol/L should provide polymers with narrower polydispersities.

Fig. 9 is similar to Fig. 7, but it takes into account deviations caused by unimolecular transfer (e.g. transfer to counterion). The plots in Fig. 9 were calculated using the following equation²²:

$$DP/DP_{id} = 1/\{1 + \ln[1/(1-p)] \cdot (k_{tr}/k_p)/[I]_0\} \quad (4)$$

for various values of parameters $b = (k_{tr}/k_p)/[I]_0$.

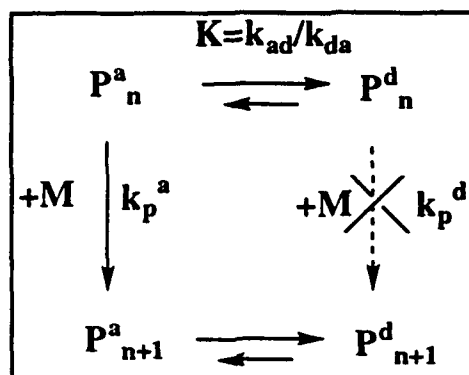
Fig. 9

Because the rate of transfer to counterion is independent of monomer concentration, whereas the rate of propagation decreases with conversion, lower molecular weights and large increases in polydispersity are expected at high conversion^{8,21}. This explains the pronounced deviation at the end of the polymerization. However, this is often experimentally undetected as the precipitated polymer is analyzed rather than the entire reaction mixture which includes oligomeric products.

5. Slow Exchange

Exchange between ions and ion pairs of different reactivities has been carefully analyzed in anionic systems and small broadening of polydispersities was used for the evaluation of the dynamics of the exchange.^{10,23} When exchange becomes slower, as in the case of aggregation of ion pairs, then polydispersities are higher and the distribution may become bimodal²⁴. Slow exchange is also one of the reasons for the high polydispersities obtained in coordination polymerizations, especially heterogenous systems.

Fig. 10 presents the results of the Monte Carlo simulations for a binary system consisting of dynamically exchanging active (P^a) and dormant (P^d) species. (The signal of the unreacted initiator was deleted from the simulated traces.) Dormant species can not react directly with monomer ($k_p^d=0$) and they are present in 1000 fold excess over active species ($K=10^3$).



Scheme 3. Polymerization in Systems with Active and Dormant Species

Figs. 10 shows the effect of the dynamics of exchange on molecular weights and molecular weight distributions. Values of the equilibrium and rate constants were assumed to be equal for the initiator and macromolecular species. If the rate of conversion of active to dormant species is higher or comparable to that of propagation (10A: $k_p^a=10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{ad}=10^7 \text{ s}^{-1}$; 10B: $k_p^a=10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{ad}=10^5 \text{ s}^{-1}$), then narrow MWD and degrees of polymerization defined by the ratio of the reacted monomer to that of the introduced initiator are obtained. Using $[M]_0=1 \text{ mol/L}$ and $[I]_0=0.01 \text{ mol/L}$, $DP_n=10, 50$, and 90 are predicted at 10, 50 and 90% conversion respectively. These values are indeed observed in Figs. 10A and 10B. Polydispersities are slightly broader. For example, $M_w/M_n = 1.12, 1.02$ and 1.01 in Figure 10A,

and 1.30, 1.05 and 1.025 in Figure 10B at 10, 50 and 90% conversion, respectively.

Fig. 10

On the other hand, if the temporary deactivation of the growing species becomes slower than propagation (10C: $k_p^a=10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{ad}=10^3\text{s}^{-1}$; 10D: $k_p^a=10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{ad}=10^2 \text{ s}^{-1}$), the molecular weights are higher than predicted (due to incomplete initiation and polydispersities are also much broader. In Fig. 10C, $\text{DP}_n=110, 108$ and 104 and $M_w/M_n = 1.99, 2.00$ and 2.04 were calculated for 10, 50 and 90% conversion, whereas in Fig. 10D, $\text{DP}_n=1040, 820$ and 480 and $M_w/M_n = 2.00, 2.08$ and 2.73 were calculated for 10, 50 and 90% conversion.

This demonstrates the surprising result that molecular weights can decrease with conversion in a living polymerization! That is, no transfer nor termination are present, and even the rate of initiation was considered equal to that of propagation. This strange and unexpected result is due to the slow reversible deactivation of the active species.

Figures 11 and 12 show the variation of MWD with conversion and as a function of the final polymerization degree for a system with exchanging active and dormant species. This could happen in cationic, anionic, radical, coordination and other polymerization systems. The MWD is unimodal but its breadth depends on the ratio of the rate constants of propagation and deactivation of active to dormant species (k_p^a/k_{ad}).

Fig. 11

Fig. 12

Polydispersities continuously decrease with conversion and with increasing chain length in contrast to systems dominated by transfer. At faster exchange (lower value of k_p^a/k_{ad}) there is a higher number of exchange events during chain growth, leading to a more uniform distribution. Similarly, at lower concentration of growing species ($[I]_0 - [I]$), longer chains with more narrow MWD are formed, according to eq. 5:

$$DP_w/DP_n = 1 + 1/DP_n + c \cdot (2-p)/p \quad (5)$$

where $c = ([I]_0 - [I]) \cdot (k_p^a/k_{ad})$.

Figure 12 demonstrates how the polymerization degree affects polydispersity at complete conversion according to eq. 6;

$$DP_w/DP_n = 1 + 1/DP_n + d/DP_n \quad (6)$$

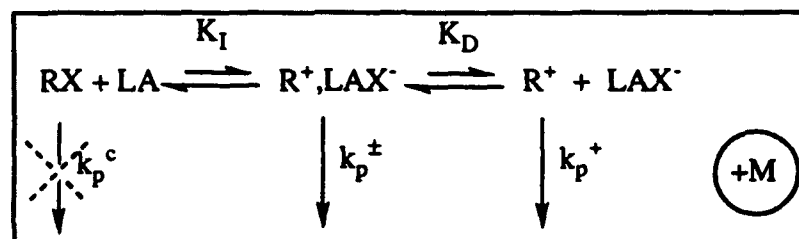
where $d = [M]_0 \cdot (k_p^a/k_{ad})$.

For example, high polydispersity ($DP_w/DP_n = 3$) is predicted for a system with $d=20$ at $DP=10$, but is reduced to $DP_w/DP_n = 1.2$ at $DP=100$. This demonstrates that in order to obtain lower polydispersities longer chain lengths must be reached in systems with slow deactivation. Of course, transfer may become significant at such high molecular weights and polydispersity may increase after its initial decrease. A typical feature of systems with slow exchange is that polydispersities decrease with conversion and with chain length in contrast to systems dominated by transfer.

6. Slow Exchange in Carbocationic Systems

Slow exchange, in addition to transfer, is the most important parameter affecting polydispersity in carbocationic polymerizations^{25,26}. It is the main reason for polymodal molecular weight distribution. It is intuitively easy to imagine bimodal molecular weight distribution (MWD) when two species of different reactivities do not exchange or exchange slowly in comparison with propagation as clearly demonstrated for anionic systems. Kinetic studies of model and macromolecular systems show that the reactivities of ions and ion pairs are similar in carbocationic polymerization and dormant species are inactive^{27,28,29,30}. The question remains, however, whether or not a bimodal MWD is possible for two species with the same reactivities. The answer is yes, if their lifetimes are different^{31,32}.

Fig. 13 shows the evolution of molecular weights with conversion for a hypothetical system, in which ions and ion pairs have the same reactivities ($k_p^+ = k_p^\pm = 10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$), covalent species are inactive ($k_p^c = 0$), the ionization equilibrium constant is $K_I = 10^{-5} \text{ mol}^{-1} \cdot \text{L}$, and the dissociation constant is $K_D = 10^{-6} \text{ mol/L}$. K_I is defined by the ratio of the rate constant of ionization of covalent species by Lewis acid, to that of recombination of ion pair ($K_I = k_i/k_r$). K_D is defined by the ratio of the rate constant of dissociation of ion pair to that of association of free ions ($K_D = k_{\text{dis}}/k_{\text{ass}}$):



Scheme 4. Equilibria in Carbocationic Polymerizations

Initial conditions are: $[M]_0=1$ mol/L, $[I]_0=0.01$ mol/L and $[LA]_0=0.1$ mol/L. These conditions, which are typical of the polymerization of styrene and some other alkenes,^{33,34,35} should lead to average values of $DP_n=10, 50,$ and 90 at conversions $10\%, 50\%,$ and 90% , respectively, provided that initiation is quantitative.

Fig. 13

Figure 13 clearly demonstrates that although ions and ion pairs have the same reactivities, bimodal MWD is obtained when no common anion (13A) or when only a very small amount of the anion is added (10^{-6} M; 13B). The low molecular weight (LMW) peak increases progressively with conversion. The number average degree of polymerization of the LMW peak increases for the case A from 1.5 to 4.6 and to 9.8 and for case B from 5.1 to 25.8 and to 49.8 with conversion (10%, 50% , and 90%, respectively). The polydispersity of the LMW peak stays fairly narrow ($M_w/M_n=1.26, 1.21$ and 1.09 for A and $1.20, 1.05$ and 1.04 for B, respectively).

The high molecular weight (HMW) peak varies much less than the LMW peak and its number average degree of polymerization decreases for case A from 1,020 to 750 and to 460, and for case B it increases with conversion from 120 to 130 and 140. (The determination of DP_n for case B is less precise due to peak overlap.) Polydispersities of the HMW peak increase for case A from $M_w/M_n=2.2$ and 2.1 to 2.54 , but decrease for case B from $M_w/M_n=1.74$ and 1.43 to 1.32 , respectively.

The overall number average degree of polymerization increases with conversion from 17(A; 11 for B) to 50 and 90 as expected for nearly complete initiation. The overall polydispersities decrease for case A from

$M_w/M_n = 120$ to 30 and to 12, and for case B from $M_w/M_n = 11$ to 2.5 and to 1.6, respectively.

On the other hand, when the concentration of the common anion is increased 10 times to the concentration $[A^-] = 10^{-5}$ mol/L a nearly perfectly behaved system is found. This leads to degrees of polymerization corresponding exactly to those for the quantitative initiation (10, 50, 90 at 10, 50 and 90% conversion). The polydispersities are also low: $M_w/M_n = 1.2$, 1.05 and 1.02, respectively.

The dramatic effect of adding a common ion shown in Fig. 13 is caused mainly by the reduction of the lifetime of free ions, since the rate of unimolecular deactivation of ion pairs is fast enough in this case ($k_r = 10^7 \text{ s}^{-1}$) compared to propagation ($k_p = 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$). On the other hand, deactivation of free carbocations is bimolecular and depends on the concentration of the anion. Under the conditions simulated in Fig. 13A, the stationary concentration of ion pairs is $[P^\pm] \approx 10^{-8}$ mol/L and the stationary concentration of free ions $[P^+] = [A^-] \approx 10^{-7}$ mol/L. Thus, providing that association is diffusion controlled ($k_{ass} \approx 10^9$ mol/L) the lifetime of free cation is defined by eq. 7.

$$\tau^+ = 1/(k_{ass} \cdot [A^-]) \approx 10^{-2} \text{ s} \quad (7)$$

During that time a free carbocation can propagate 1000 times and form high molecular weight polymer (eq. 8).

$$\text{DPH} = k_p^+ \cdot [M] \cdot \tau^+ \approx 10^3 \quad (8)$$

The life time of an ion pair is much shorter (eq. 9).

$$\tau^{\pm} = 1/(k_r) \approx 10^{-7} \text{ s} \quad (9)$$

with less than one propagation step possible during one ionization period at $[M]=1 \text{ mol/L}$. Thus, the population of ion pairs grows steadily and continuously, providing a polymer with narrow MWD.

Fig. 14 shows the effect of both ionization and dissociation equilibria on MWD of polymers without added salts with common anions at 90% conversion with a standard recombination rate constant $k_r=10^7 \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$. The bottom three traces and top three traces depict the change in K_D from 10^{-5} to 10^{-7} mol/L for two different ionization equilibrium constants $K_I=10^{-5}$ (bottom) and $10^{-3} \text{ mol}^{-1}\cdot\text{L}$ (top), respectively.

Fig. 14

When ionization is weak, a clear bimodal MWD is observed. The concentration of ion pairs equals $[C^{\pm}]=10^{-8} \text{ mol/L}$, whereas the concentration of free ions changes from $[C^+]=0.3 \cdot 10^{-7}$, 10^{-7} and to $3 \cdot 10^{-7} \text{ mol/L}$. This means that the proportion of monomer consumed by ions increases from $\approx 76\%$ to 90% and to 97% , respectively. This is seen in the relative proportions of HMW and LMW peaks.

For the stronger ionization ($K_I=10^{-3} \text{ mol}^{-1}\cdot\text{L}$), the concentration of ion pairs equals $[C^{\pm}]=10^{-6} \text{ mol/L}$, and the concentration of free ions varies from $[C^+]=0.3 \cdot 10^{-6}$, 10^{-6} and to $3 \cdot 10^{-6} \text{ mol/L}$. This means that the contribution of free ions increases from approximately 25% to 50% and then 75% , respectively. In trace 4, the 25% contribution of free ions can hardly be seen without magnification (broad MWD). In trace 5 nearly equal proportions of both peaks are seen, whereas in trace 6, free ions dominate but differences between polymerization degrees are so small that peaks can not be separated.

The fraction of the LMW peak is determined by the proportion of ion pairs among all carbocations. However, if they exchange very rapidly with covalent species they can not be distinguished from dormant species and the average DP_n of LMW is in that case defined by the ratio of concentrations of the monomer reacted with growing ion pairs to the concentration of covalent species (approximately equal to that of the initiator, provided that initiation is complete). Thus, DP_n of LMW is determined by eq.10.

$$DP_n^L = \Delta[M]/([I]_0 - [I]) \cdot \{[C^\pm]/([C^+] + [C^\pm])\} \quad (10)$$

The molecular weight of this fraction grows progressively with conversion and MWD is rather narrow ($M_w/M_n < 1.2$), but depends on the dynamics of exchange as discussed previously.

DP_n of the HMW fraction is more difficult to estimate. DP formed during one activation period depends on the relative rates of propagation and deactivation of free ions (the association process) (eq. 11).

$$\begin{aligned} DP_n^H &= R_p/R_{ass} \cdot \{[C^+]/([C^+] + [C^\pm])\} = \\ &= k_p[M]/k_{ass} \cdot [C^+] \cdot \{[C^+]/([C^+] + [C^\pm])\} \\ &= k_p[M]/\{k_{ass}([C^+] + [C^\pm])\} \end{aligned} \quad (11)$$

Surprisingly, the DP_n of the HMW peak does not depend on the concentration of ions rather than on the total amount of ionic specie as shown clearly in Fig. 14 shows that quite clearly. The decrease of DP_n^H in traces 1,2,3 is due to increasing total concentration of carbocations from $4 \cdot 10^{-8}$ to $1.1 \cdot 10^{-7}$ and to $3.3 \cdot 10^{-7}$ mol/L. The values of DP_n^H in traces 1,2,3 in Fig. 14 agree well with those predicted from eq. 11, assuming one single

activation process for this fraction: $DP_n^H=1200, 500, 200$. On the other hand, the values of DP_n^H in traces 4, 5, 6 are in the range 100 to 200 and are much higher than those predicted for one single activation process for this population : $DP_n^H= 80, 20$ and 12, respectively. This indicates that this population must grow with conversion in contrast to the changes shown in traces 1, 2, 3. The repetitive activation processes also lead to more narrow MWD for this fraction which in traces 6 is $M_w/M_n=1.30$ for both free ions (75%) and ion pairs (25%).

Conclusions

Scheme 5 summarizes the effect of various imperfections such as slow initiation, termination, transfer and slow exchange on kinetics, molecular weights and polydispersities

	Rate	MW	MWD
slow initiation	slower than ILS (but with acceleration)	initially higher, but approaches ILS	<1.3
termination	slower than ILS (with deceleration)	no effect (limited conversion)	broader than ILS
transfer	no effect	lower than ILS	broader than ILS
slow exchange	no effect	?? (polymodal)	very broad, polymodal

Scheme 5. Effect of k_i , k_t , k_{tr} , and k_{ex} on Kinetics and MW in Comparison with an Ideal Living System (ILS).

The simulations presented in this paper demonstrate that well defined polymers can be prepared in systems with chain breaking reactions present. Thus, nonliving polymerizations may provide controlled polymers under carefully selected conditions. On the other hand, polymers with unpredicted molecular weights and broad or even polymodal molecular weight distributions may form in living systems without irreversible transfer and termination. As shown in Fig. 10, the molecular weights may stay constant or even decrease with conversion in some living systems. Therefore, the differences between living and controlled polymerization outlined in Scheme 1 must be stressed.

Acknowledgments

Financial support from the National Science Foundation, the Office of Naval Research and the donors of the Petroleum Research Foundation is highly appreciated.

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Captions for Figures

Fig. 1. Effect of various ratios $R_i=k_p/k_i$ on kinetics for slow initiation.

Fig. 2. Dependence of DP_n on conversion for various ratios $R_i=k_p/k_i$.

Fig. 3. Dependence of DP_n on conversion for various ratios $R_i=k_p/k_i$ during 4 consecutive monomer additions for slow initiation.

Fig. 4. Effect of various ratios $R_t=k_p/k_t$ on kinetics.

Fig. 5. Dependence of DP_n , DP_w and DP_w/DP_n on conversion for termination by coupling in a radical polymerization with constant initiation rate.

Fig. 6. Dependence of DP_n on conversion for various ratios $R_{trM}=k_p/k_{trM}$ for transfer to monomer.

Fig. 7. Effect of parameter $a=(k_{trM}/k_p) \cdot (\Delta[M]/[I]_0)$ on deviation from ideal behavior for transfer to monomer.

Fig. 8. Dependence of MWD on various ratios "a" for transfer to monomer.

Fig. 9. Effect of parameter $b=(k_{tr}/k_p)/[I]_0$ on deviation from ideal behavior for unimolecular transfer (e.g. to counterion).

Fig. 9. MWD in cationic polymerization as a function of conversion; $[M]_0=1$ M, $[I]_0=0.01$ M, $[LA]_0=0.1$ M; $k_p^+=k_p^\pm=10^5$ M⁻¹s⁻¹; $K_D=10^{-7}$ M; $K_I=10^{-5}$ M⁻¹; $k_i=10^2$ M⁻¹s⁻¹.

Fig. 10. The effect of the dynamics of exchange between active and dormant species on the evolution of MW and MWD with conversion; $[M]_0=1$ M, $[I]_0=0.01$ M; $k_p^a=10^5$ M⁻¹s⁻¹, $k_p^d=0$ M⁻¹s⁻¹; $K=10^{-3}$;
A: $k_{da}=10^4$ s⁻¹, $k_{ad}=10^7$ s⁻¹; B: $k_{da}=10^2$ s⁻¹, $k_{ad}=10^5$ s⁻¹; C: $k_{da}=1$ s⁻¹, $k_{ad}=10^3$ s⁻¹; D: $k_{da}=10^{-1}$ s⁻¹, $k_{ad}=10^2$ s⁻¹;

Fig. 11. Effect of parameter $c = ([I]_0 - [I]) \cdot (k_p^a/k_{ad})$ on evolution of polydispersities with conversion.

Fig. 12. Effect of parameter $d = [M]_0 \cdot (k_p^a/k_{ad})$ on evolution of polydispersities with chain length at complete conversion.

Fig. 13. MWD in carbocationic polymerization as a function of conversion in the presence of common anion; $[M]_0 = 1$ M, $[I]_0 = 0.01$ M, $[LA]_0 = 0.1$ M;; $k_p^+ = k_p^\pm = 10^5$ M⁻¹s⁻¹; $K_D = 10^{-6}$ M; $K_I = 10^{-5}$ M⁻¹; $k_i = 10^2$ M⁻¹s⁻¹; $k_r = 10^7$ s⁻¹; A: no salt, B: $[A^-]_0 = 10^{-6}$ M, C: $[A^-]_0 = 10^{-5}$ M (all conditions except common ion identical to those in Fig. 11).

Fig. 14. MWD in carbocationic polymerization as a function dissociation and ionization equilibrium constants; $[M]_0 = 1$ M, $[I]_0 = 0.01$ M, $[LA]_0 = 0.1$ M; $k_p^+ = k_p^\pm = 10^5$ M⁻¹s⁻¹; $k_r = 10^7$ s⁻¹; 1: $K_D = 10^{-7}$ M, $K_I = 10^{-5}$ M⁻¹; 2: $K_D = 10^{-6}$ M, $K_I = 10^{-5}$ M⁻¹; 3: $K_D = 10^{-5}$ M, $K_I = 10^{-5}$ M⁻¹; 4: $K_D = 10^{-7}$ M, $K_I = 10^{-3}$ M⁻¹; 5: $K_D = 10^{-6}$ M, $K_I = 10^{-3}$ M⁻¹; 6: $K_D = 10^{-5}$ M, $K_I = 10^{-3}$ M⁻¹.

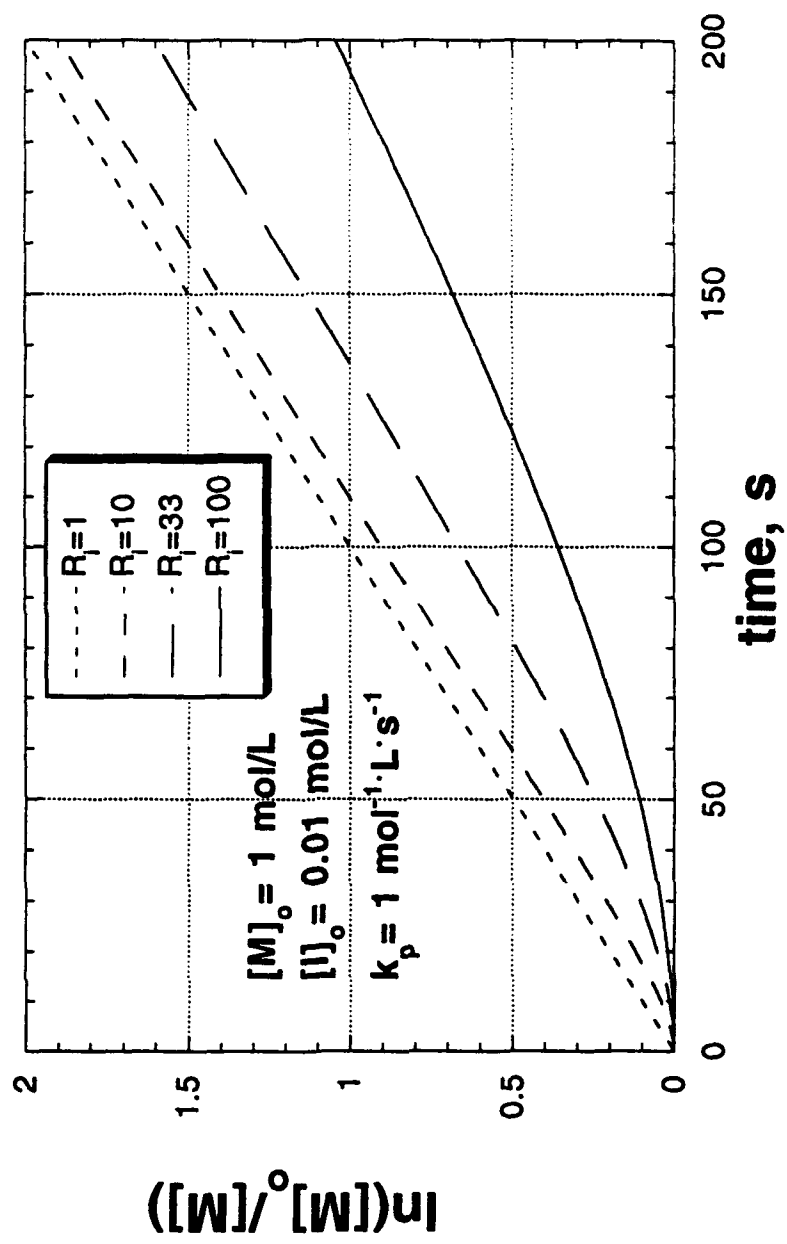


FIG. 1

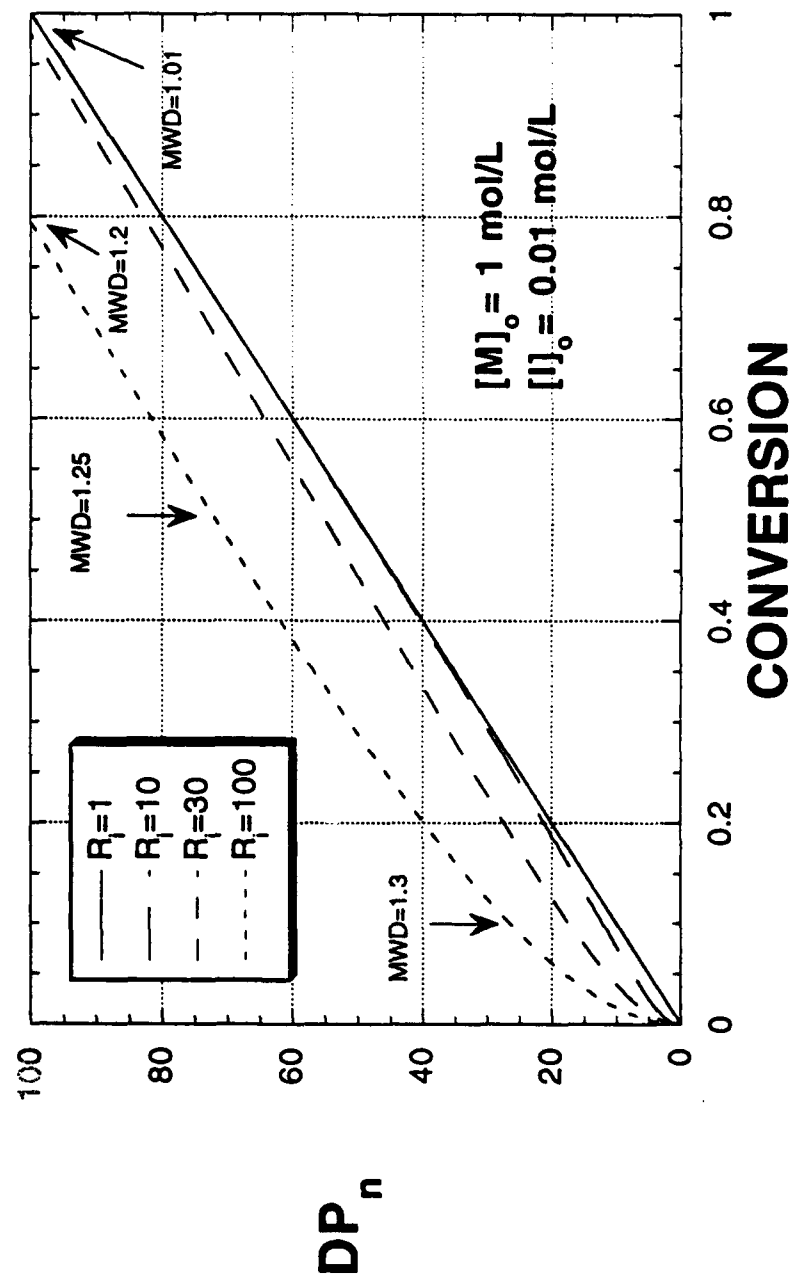


FIG. 2

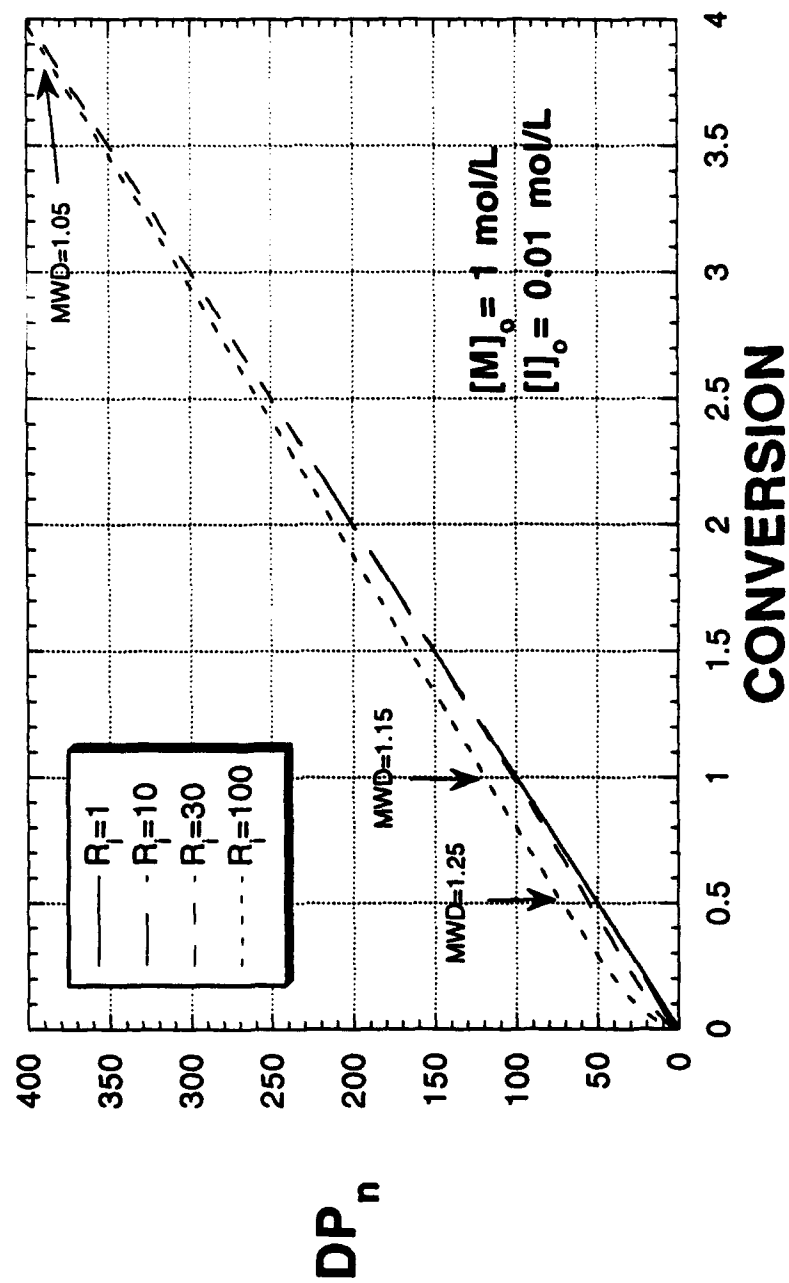


FIG. 3

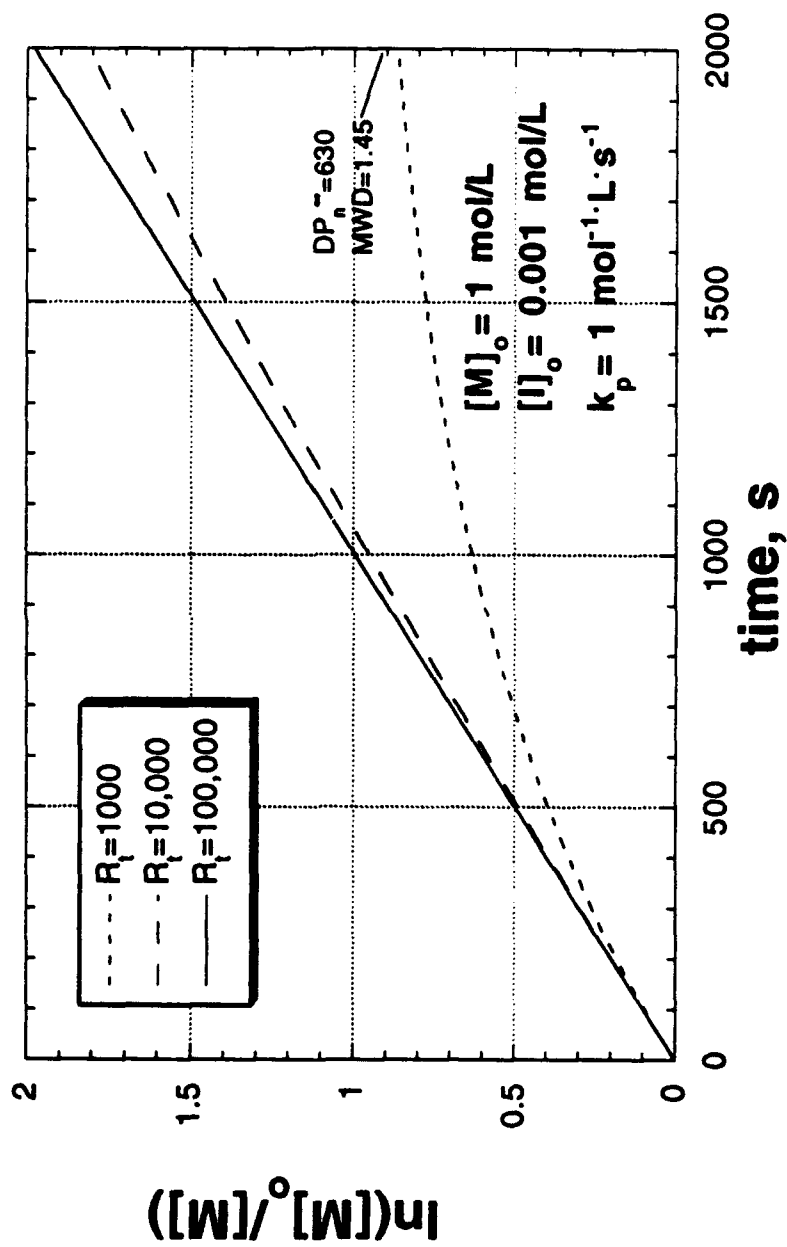
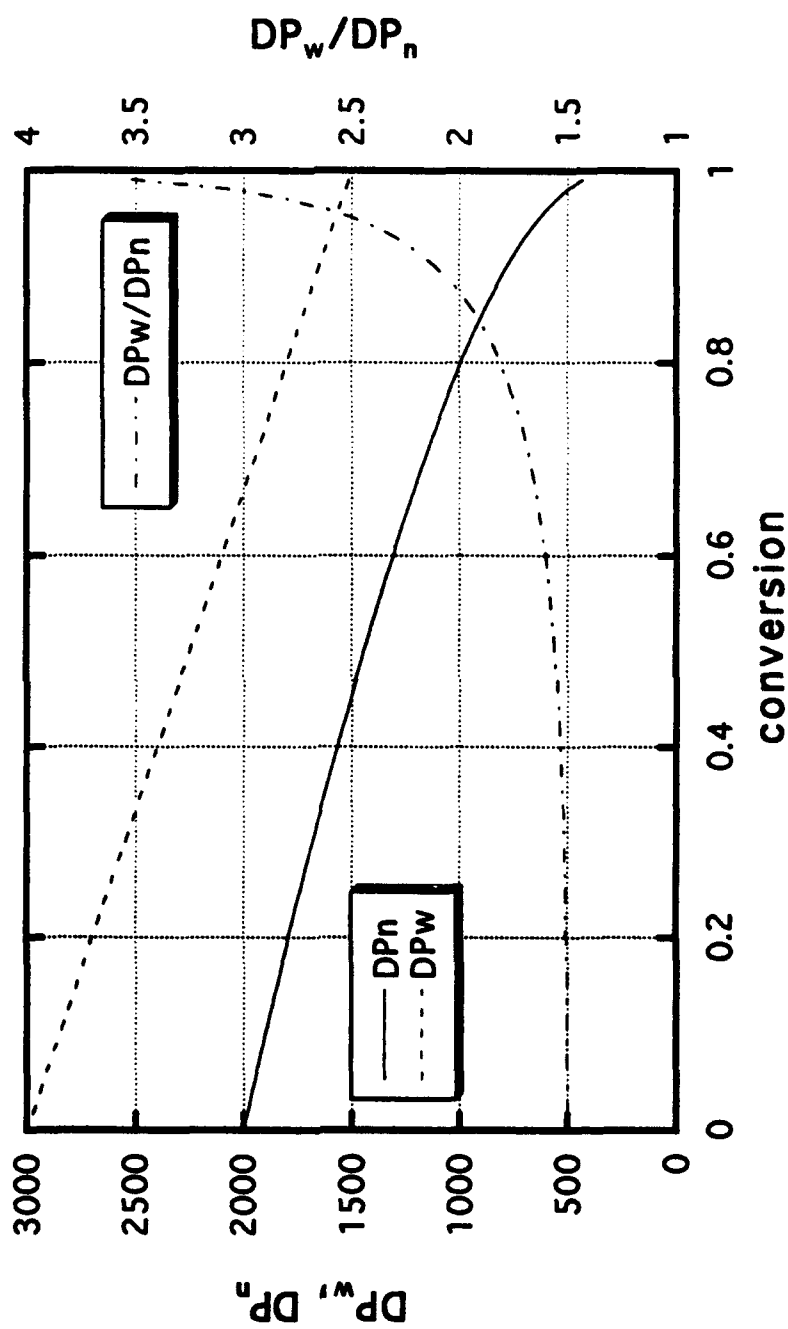


FIG.4



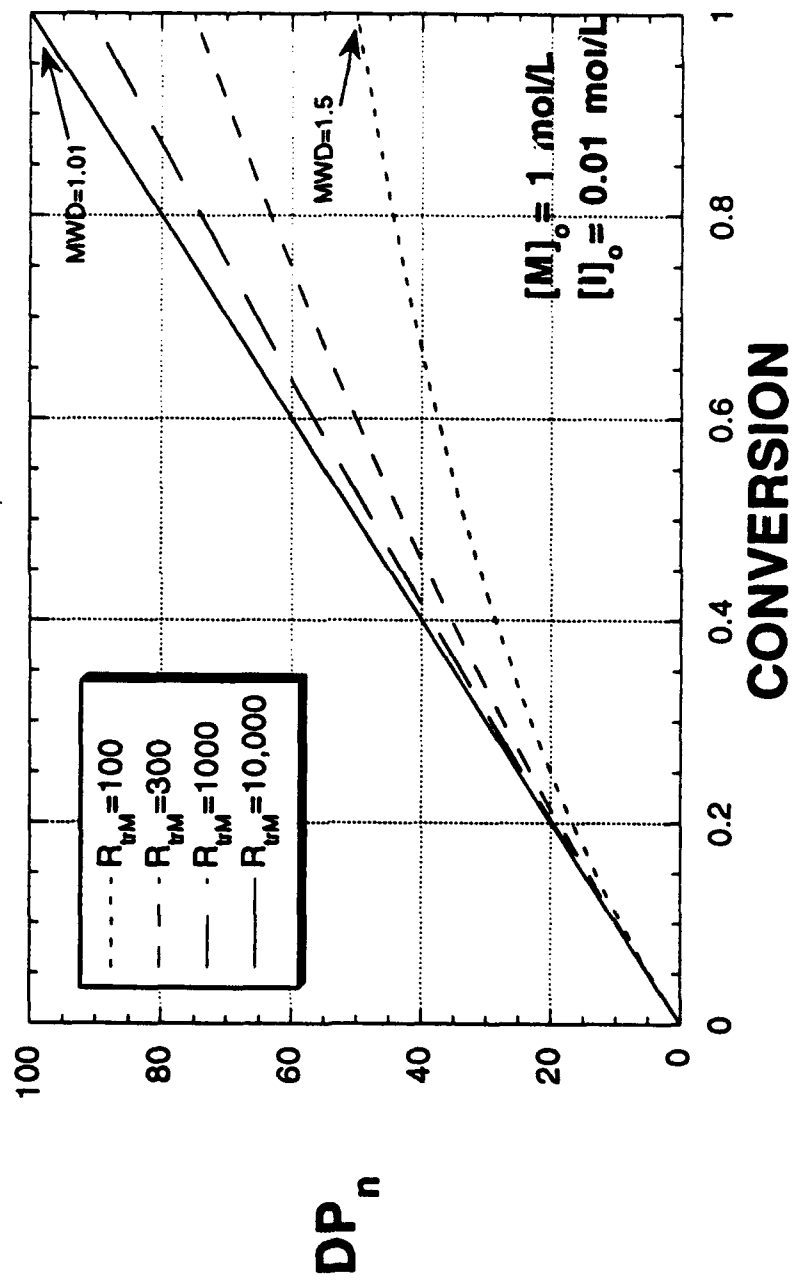


FIG. 6

